Chapter 17. Micro/nano-capsules for anticorrosion coatings

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Content

Abstract

In the last decade, the interest in the self-healing and slow release coatings applied against corrosion increased dramatically as it helps to expand duration of coating and, at the same time, to increase the structural materials' life. In these types of paints are micro and nanoncapsules that enable the reparation of the coating upon exposure to external stimuli like mechanical degradation, changes in the pH and/or temperature. In spite of the extensive laboratory research work, there are many unsolved problems in understanding the function of smart coatings. To summarize the knowledge accumulated up-to-now in this topic will help both academic and industrial specialists to keep in center of interest for further research to solve problems that will result in development of more effective micro- and nanocontainers for different paints. Coatings with micro- and nano-containers/capsules improve the basic coating characteristics like anticorrosion efficiency. The chapter first discusses the importance of self-healing and slow release phenomena, and then it focuses on the basic knowledge of micro- and nano-capsule preparation techniques as well as on the importance of "filled" capsules. Advances on preparation of different types of the containers (organic, inorganic, and multilayer) are reviewed. Then the shell and wall materials, the wall thickness and its mechanical properties is discussed as one of the most important questions. One must keep in mind that the capsules must remain intact for years during storage, coating formulation and application and, additionally, in the dry coating. Experimental techniques used for characterization of micro/nanocapsules (size, size distribution, mechanical stability etc.) are discussed.

Key words: micro-/nano-capsules, self-healing, corrosion inhibition, nanocontainers, coatings.

17. Micro/nano-capsules for anticorrosion coatings

17.1. Introduction: *anticorrosion coatings*

Corrosion is a serious problem all over the world. The cost of corrosion includes materials for reparation of corrosion damage, the reduced capacity of equipment and the manpower to repair it increases. The corrosion problems could be solved by protective layers that ensure the integrity of the metal. However, even the best protective coatings can allow the diffusion of oxygen, the admittance of aggressive chemicals and moisture to the metal surface; the coating could delaminate from the solid surface and, as a consequence, the dissolution of metal starts. The first signs of the corrosive attack are cracks and pits formed on the solid surface. The problem could be solved or mitigated by coatings that are tailored for protection against corrosion and any other undesired external interaction. They ensure a long-term performance of solids.

There are great varieties of protective coatings (metallic, inorganic, organic) which are used to protect the surface damages caused by corrosive environment.

Anticorrosion coatings could be classified according to their activity, like sacrifice and barrier coatings. In the case of sacrificial coatings, an additional metal layer corrodes instead of the base metal. The barrier films should be non-porous; this is how they save the metal from corrosion. Polymers can provide thick barrier layers applied mainly at atmospheric and in aggressive environment. Anticorrosion coatings are the most widely used protection through the barrier properties, and inhibit the contact between chemical environment and the materials exposed to corrosion. The best coatings for corrosion protection provide not only a barrier between the metal and the environment, but, on demand, it could release smart additives, like corrosion inhibitors continually at the damaged place. Other undertakings can improve the efficiency of coatings like in case of those paints that involve special additives with efficient inhibitors – like microcapsules.

17.2. Smart coatings: Applications of micro- and nanocapsules in self-healing coatings: *chemical and physical aspects of self-healing.*

Smart coatings that form special films of pre-defined properties, allow relevant protection against the environmental undesired impacts, contain programmable materials with special electrical, physical, chemical and mechanical properties that allow spontaneous respond to external stimuli (chemical, mechanical, heat etc.). It is significant to emphasize that smart anticorrosion coatings

have special functionalities like pH-sensing, warning ability on unwanted risk, bringing into effect corrosion inhibition and repair. In other words, they are able to detect and prevent corrosion, and on-demand they deliver corrosion inhibitors. This protective effect can be achieved by incorporation of different additives in the coating, like inhibitors in the self-healing and multifunctional microcapsules as well as pH-triggers. Smart coatings remain passive until the external stimuli, when, according to the environmental effect, they react and perform the function according to the impact. The most important characteristics of the smart coatings are that they do not need frequent inspection, the maintenance cost decreases, the lifetime of the instrument/equipment increases.

For mechanical damages, methods for autonomic repair techniques were developed in the first decade of the two-thousand years. From that time, enormous increase in publications appeared in the literature about the self-healing technique. Smart coatings with self-healers for corrosion protection have attracted immense interest in the last decade because of ability to recover the structural integrity of the coating film after mechanical or other damage, and due to the capability to prevent crack propagation by releasing active materials from micro- and nanocapsules. The smart coatings are based on controlled release of active materials (pH triggers, corrosion indicators/inhibitors). The corrosion responsive micro/nanocapsules (M/NCs) detect the chemical changes generated by corrosion and they release the core materials from the capsules.

One must keep in mind that the development of the self-healing process is inspired by the nature. The living organisms are able to recover from injuries and to resume active and reproductive functions. In self-healing coatings, the incorporated M/NCs will let free the reactive core agents on external stimuli, which will heal the damaged film, like in the real life. But in these cases the M/NCs are synthetic materials in function and they do not have any metabolic attribute.

The best strategy to achieve self-healing ability is the application of M/NCs that are uniformly entrapped into the coating. In this way the undesired interaction between the active component and the passive matrix can be avoided. When the local environment undergoes changes or an outer impact affects the surface of capsule, the M/NCs respond to this signal and release the encapsulated active core material to heal the damaged surface (Shchukin and Möhwald, 2007). Microcapsules synthesized with reactive core materials function after the damage of the coating and this is how the coatings modified with M/NCs exhibit excellent corrosion protection.

Nanocontainers with the ability to release the capsulated active chemicals in a controlled way or at controlled rate are involved in self-repairing/self-healing multifunctional coatings. Depending on the nature of the sensitive components of the shell material, controlled release could also be introduced into the shell, which could be reversible or irreversible (tunable permeability or total rapture). In case of porous shell wall there is a continuous and controlled release of the active component. This is the so-called slow-release activity.

17.2.1. Advantages of encapsulation of active materials

The active chemicals in the core of the capsule are isolated from the other components of the paint; therefore, they are activated only on external stimuli. The encapsulation reduces the environmental impact. The preparation of micro/nanocapsules is simple, the materials used are economic, and the chemical processes are simple. Considering the chemical and physical aspects of self-healing two stages are particularly important:

- how can the active material from the ruptured M/NCs get into the wounded area?
- how will the healing material at the damaged area cover the gap and re-bond?

Kinetic and thermodynamic parameters will control these processes (diffusion of polymer molecular chain ends, re-bonding). An example is: when reactive free radicals are quenched by oxygen, by water or by other chemicals then re-bonding will happen. Diffusion, inter-diffusion can help in repair (Yang et al., 2015). It is evident, that the kinetic energy of polymer chains and the entropic changes during the diffusion will determine the reparation (Yang and Urban, 2013). An important factor is the presence of free volume in achieving a desirable mobility of polymer chains (Simha and Boyer, 1962). The free volume could be described as an average chain mobility, which is reflected in the glass transition temperature. In a self-healing system, the length scale of heterogeneity is critical. At Angstrom (Å) level self-healing will happen by reforming bonds at site of chain of cleavage place. Formation of block, branched and star polymers at nano-/microscale via micro-phase separation facilitates the self-healing (White et al., 2001).

When a self-repairing material is planned, it is important to understand which chemicals are capable to cleave due to mechanical damage and to plan networks with localized segmental

mobility, as well as to try to synchronize re-bonding dynamics with physical rearrangements of macromolecular reactive segments.

17.2.2. Chemical aspects of the self-healing.

In most cases the core material consists of chemicals applicable for polymerization (e.g. linseed oil) applied together with other additives that help in polymerization; when the liquid fills the damaged place, the complete coverage saves the metal form the outer corrosive effect. In case of the chemical aspects of the self-healing we have to consider that the chain mobility is limited and bond reformation ability is missing. In the last decade, several reactions were elaborated to help in the self-repairing through cleavage and reformation of specific bonds. These stimuli responsive components are involved into the polymer and are characterized as reversible covalent bonds (cycloaddition, exchange reaction, free radical reaction) and non-covalent bonds (hydrogen bonds, metal-ligand coordination, π-π stacking and ionic interactions, host-guest interaction). An example is the presence of -S-S- bond in the polymer, which could be either in an epoxy resin, or in an organic-inorganic polyurethane hybrid (Aguirresarobe et al., 2017; Yang et al., 2015).

Additionally, to those examples when the self-healing is achieved through special component built-in the polymer matrix, other very important strategy for improving the self-healing phenomenon of coatings is the application of M/NCs. Their distribution in the passive matrix should be uniform and when the local environment undergoes changes or when the surface is affected by outer influence, they must respond on the outer signal with release of encapsulated active materials and they have to heal the crack (Shchukin and Möhwald, 2007).

In a coating with M/NCs there are several subjects for discussion. One is that the M/NCs have a solid shell (with or without pores) and inside the core contains active materials that could be very different (solid, liquid, gas).

The benefits of the microcapsule applications and the core-shell structure can be summarized as follows: when the core material is sensitive or unstable, the shell will protect it from the pre-mature degradation/altering. When its solubility and dispersion-ability could be improved, the process ability is better.

In other case the spheres have a matrix structure built of different solid materials. In this case, the active chemicals are “filled” into this porous structure and the active agent will continuously have scattered during the application.

17.2.3 Materials applicable for shell.

What is expected from the shell material to have good compatibility with the core material and with components of the coating as well; i.e. in a water-born paint the shell wall surface is hydrophilic, in a solvent-born one mainly hydrophobic. It means that the core material should stay intact, be released only on some outer stimuli, which could be heat, mechanical impact, or chemical influence.

The shell is generally built-up from different polymers. The most frequently used composites of shell materials is the urea-formaldehyde alone or in combination with other co-monomer (Brown et al., 2003; Chung et al., 2017; Jadhav et al., 2011).

Several chemicals like polyurethans, polystyrenes, melamine resins, poly-siloxanes, poly-acrylates, and some other copolymers applicable for shell material are summarized in several publications (Mac et al., 1989; Nardello-Rataj and Leclercq, 2014; Tong et al., 2010; Wu et al., 2014). There are combined shell components like silica/poly-urea (Wu et al., 2014). An interesting example is when poly-sulfone is the shell material (filled with tung oil) (Li et al., 2017). The capsules synthesized by solvent evaporation method, embedded in epoxy coating, show not only good anticorrosion activity but high thermal stability as well.

17.2.4. Micro-/Nano-encapsulation techniques.

The microencapsulation techniques are either chemical (polymerization: suspension, dispersion poly-condensation), or physical/physico-chemical (coacervation, layer-by-layer assembly, sol-gel encapsulation, supercritical CO_2-assisted microencapsulation) or physico-mechanical (spray drying, multiple nozzle spraying, fluid-bed coating, centrifugal technique, vacuum encapsulation, electrostatic encapsulation).

Among the chemical methods the *in-situ* processes (emulsion-, suspension-, precipitation- or dispersion-) polymerization and interfacial poly-condensations are the mostly used chemical techniques for microencapsulation (Gite et al., 2015; Luna-Xavier et al., 2001; Marathe et al.,

2015; Okubo et al., 2003; Szabó et al., 2011). In these reactions, solid layers are formed around the active cores (Smadzadeh et al., 2010). Generally, the core material is emulsified in a proper non-miscible medium and either a water-in-oil or oil-in-water micro-/nano-emulsion is formed. In the case of emulsion polymerization, the shell forming chemicals are dissolved in the continuous phase; in other cases, i.e. in interfacial polymerization, both the continuous and non-continuous phases contain these chemicals and the polymeric layers are formed at the oil/water interface (Thanawala et al., 2014).

A number of publications summarize the synthesis of M/NCs as well as they pointed out the most important factors (concentration, mixing speed, temperature, solvents, other additives) that influence the size, size distribution, shell wall thickness. With decreasing concentration of monomers and increasing mixing ability, the M/NCs diameter will decrease. The type, shape and speed of the mixing apparat are important as all these factors will determine the capsule size and its distribution. The ratio between monomers and additives in the reaction – together with other reaction conditions, will result in a thinner or thicker shell wall, which is an important characteristic of the M/NCs.

Among the physico-chemical processes, one is the coacervation method (which could be named as phase separation phenomena), which was first described in 1949 (Bungenberg de Jong, 1949). Nowadays two methods for coacervation is used, the simple and the complex processes. The mechanisms in both preparations are identical when the shell deposition happens from the aqueous phase onto an oil drop or on a solid particle.

The method of encapsulation by polyelectrolyte multilayer involves layer-by-layer electrostatic assembly of electrically charged particles which results in preparation of multilayer thin films; this is also applicable for preparation of a microcapsule shell wall. When a sol-gel deposition method is applied, generally either silica or metallic alkoxides are hydrolyzed and through a condensation reaction solid particles are formed which could be deposited onto oily drops. Fig. 17.1 shows the effect of the reaction conditions on the capsules: a. proper concentration of the reaction components, b: insufficient concentration of reaction components.

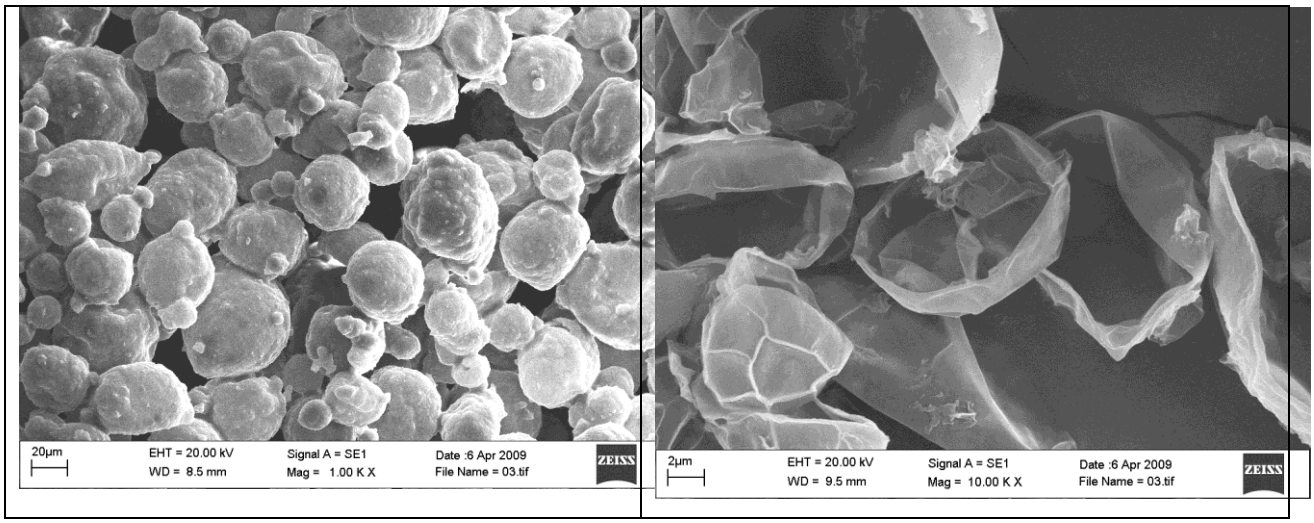

Fig. 17.1 (a,b). The effect of the reaction conditions on the capsules: a. proper concentration of the reaction components, b: insufficient concentration of reaction components.

17.2.5. The core materials in anticorrosive M/NCs.

In the healing process the most important is that on an external impact the encapsulated healing core agents are released from the capsules, move into the cracks, form polymers, and finally very quickly heal the crack via solidification. At the attempts, in most cases the microcapsules contained only one type of chemicals, mainly vegetable oil (linseed oil) or tung oil (Jadhav et al., 2011) that, after flowing out from the capsules, solidify via oxidation. This reaction, without any additive, takes too long time that's why later catalyst was also encapsulated, that helped to harden the oil in the crack in shorter time. Later attempts were done to produce efficient self-healer microcapsules with different additives, which were encompassed in the same shell, e.g. dicyclopentadiene applied together with Grubbs catalyst formed the core material (White et al., 2001).

In other cases, epoxy resin was used together with different additives (di-glycidyl ether bisphenol A and imidazole, or mercaptane hardener). Liquid di-isocyanat monomer was also encapsulated to create a one-part self-healing corrosion resistant coating (Yabuki and Okumura, 2012) then a novel organic silane (1H,1H, 2H, 2H-perfluorooctyl triethoxysilane) incorporated in poly(urea-formaldehyde) shells could control the corrosion as a self-healing agent (Huang et al., 2012). The most significant expectation from a core material is to plug the crack rapidly, to solidify quickly, and the other core materials (usually encapsulated into the same container, in some cases in other

microsphere) should assist in the reaction of the liquid oil (oxidation, polymerization etc.) and, at the same time, to inhibit the corrosion processes. These processes could be supported by other additives that are real corrosion inhibitors (e.g. amines or phosphonic acids with long carbon chain).

Another possibility is the use of a so-called pH-trigger. The corrosion is an electrochemical process, with cathodes and anodes statistically distributed on the metal surface and it leads to different pH values throughout the metal surface. In the case of localized corrosion, the anode area has an acidic, the cathode an alkaline pH environment. A pH sensitive shell material can hydrolyze and break at the change of pH caused by corrosion processes (Motornov et al., 2010; Shchukin and Möhwald, 2007). In case of anticorrosion coatings, one type of the core materials in the micro/nanocapsules incorporated into the coating is a pH-trigger material; when it is released from the capsules, it allows the early detection of corrosion. When this special core material is used together with a corrosion inhibitor, the rapture of the microcapsule not only gives a signal of the corrosion, but this undesired process is inhibited by deliver of healing agents at the same time.

When the core material is an inhibitor, it is also supposed to be released from the shell via slow dissolution; the shell wall ought to be porous which is achieved via proper shell wall synthesis.

17.2.6. Influence of the capsule parameters on the inhibition efficiency.

For microcapsules based self-healing polymer materials, self-healing performance is influenced by many factors such as size and content of the capsules. The amount of healing agent delivered in a self-healing material is determined by the product of the microcapsule weight fraction and the microcapsule diameter (capsule volume). If sufficient healing agent is delivered to fill the crack volume, the healing performance is optimized. By forming a relationship between microcapsule size, microcapsules weight fraction, and crack volume, it is possible to propose self-curing schemes that are custom-made to repair specific types of damage.

Upon damage-induced cracking in the matrix, microcapsules are supposed to release their encapsulated liquid healing agent into the crack planes. All related materials must be carefully planned and engineered. For instances, encapsulation procedure must be chemically compatible with the reactive healing agent, and the liquid healing agent must not diffuse out of the capsule

shell during its potentially long shelf-life (storage). At the same time, the microcapsule walls must be sufficiently resistant to processing conditions of the host composite, while preserving excellent adhesion with the healed polymer matrix to guarantee that the capsules rupture upon composite fracture (Williams et al., 2009).

17.2.6.1. Wall thickness.

It is clear that the mechanical rupture of the microcapsule is the important stage for the self-healing process. Therefore, it is obvious essential to manufacture microcapsules with optimal mechanical properties and wall thickness. The relationship between the hardness (stiffness) of the capsule and the one of the polymer matrix explains how the wall crack will spread in the sample.

17.2.6.2. Size and volume

The microcapsules diameter is influenced by a combination of several factors including the geometry of the mixing device, viscosity of the reaction media, surfactant concentration, agitation rate, temperature, etc. The influence of microcapsule diameter and crack size on the effectiveness of microcapsules as self-healing materials was also studied by Rule et al. (2007). The amount of liquid that microcapsules deliver to a crack face is shown to scale linearly with microcapsule diameter for a given weight fraction of capsules. In addition, self-healing performance reaches maximum levels only when sufficient healing agent is available to entirely fill the crack. It was determined that self-healing is more efficiently demonstrated with smaller microcapsules and with lower weight fractions of microcapsules.

The amount of inhibitor that microcapsules could provide to a coating crack is linearly dependent on their volume (capsules diameters), for a given weight fraction of capsules.

Moreover, the size of the microcapsule also plays a role in the performance of the system, in terms of the effect on toughness of the composite, and the nature of interface between microcapsule and polymer matrix.

The work of Brown et al. (2004) showed that smaller sized microcapsules show maximum toughening at lower concentrations while Rule et al. (2007) reported that larger sized microcapsules achieve better protection than smaller sized microcapsules, at the same weight fraction. This is seemingly due to the quantity of healing agent present in the capsules.

Reducing the size of the microcapsules may enable self-healing of smaller forms of damage like micro-cracks.

17.2.6.3. Shell wall thickness

The capsule shell wall thickness (typically between 160 and 220 nm thick) is found to be mostly dependent of production parameters. The microcapsule size is controlled primarily through the agitation speed during the encapsulation process. Typically, the agitation speed ranges between 200 and 2000 rpm. The increase of agitation speed linearly reduces the average shell thickness of the microcapsules and lowers the core fractions, and thus reducing the active agent content in the capsules (Rule et al., 2007).

Increasing the shell width of a capsule is required if the permeability or the mechanical stability of the layer is not reasonable. Shells of slow-release microcapsules in solvent-based paints must exert resistance to the solvent but should be fairly hydrophilic to guarantee water-accessibility.

17.2.6.4. Microcapsule morphology

The microcapsules morphology is another important character to be considered where spherical microcapsules produce smoother surfaces (Brown et al., 2004; Yang et al., 2008).

17.2.7. Factors that influence the applicability of the M/NCs: *Influence of single and multi-shelled microcapsules.*

The permeability and the mechanical stability, mechanical strength, friability will regulate the shell wall thickness. The reaction parameters will determine the thickness, hardness of the shell wall (Szabó et al., 2011; Telegdi et al., 2014). One must keep in mind that a too thin shell will be destroyed already during the storage or during the application of the paint. On the other hand, it is necessary to increase the shell wall thickness when the mechanical stability or the permeability of the wall is not proper. At mechanical damage, when the shell wall is too thick, the capsules will not open at the outer actions and the curing core material will not be able to heal the opened coating. Contrary to this case, a very thin shell wall opens before necessity.

This requirement (i.e. to produce micro- and nanocapsules with proper wall thickness) is achieved by different techniques, e.g. by combination of preparation both types of shell walls like hydrophilic and hydrophobic. When a shell mechanically good enough but there is a problem with the wetting characteristic or with the solvent stability, combination of shell walls, a second or third layer can solve this problem.

17.2.8. Capsule size, coating formulation.

Other important factors that influence the usefulness of the M/NCs are the capsule performance like size, size distribution. Reaction parameters influence these factors. The size of capsules could be regulated by the stirring rate and the type of stirring apparatus. In some cases, a three-bladed propeller results in proper capsule size. With increasing stirring rate (and stabilizer content at the same time) the size of microcapsules decreases. The temperature also influences the microsphere diameter. Smaller capsules could be produced at lower temperature but the reaction rate with decreasing temperature decreases, so, it is necessary to harmonize these parameters to get capsules in proper size as well as in the best yield. Another possibility is to use microwave to assist the formation of nanocapsules. But one should keep in mind the nanocapsules do not carry too much healing materials! Again, the balance between the capsule size and the self-healing usefulness is a factor the specialists should handle properly.

The size is one characteristic, the other is the size distribution. From the coating point of view, the best is when the size of capsules is in a small range.

When M/NCs are applied in coatings the capsule size should be harmonized with the dry coating thickness which is generally 100-200 μm in case of a heavy-duty anticorrosive coating and this is the upper limit on the microcapsule diameter. For poly (urea-formaldehyde (UF)) microcapsules a typical microcapsule size is 60-150 μm (Benthem et al., 2007; Nesterova et al., 2012). The size of the small containers is very important. The diameter of microcapsules should be in the range of 60-150 micrometer, and in the case of nanoparticles between 10 and 100 nm. But one has to keep in mind that they are containers with active, healing core material. When the quantity of this healer is too small, the main function could not be accomplished!

17.3. Encapsulation of corrosion inhibitors in nano-containers for self-healing coatings.

As mentioned previously, it is a noticeable increasing tendency to change the classic, most commonly used materials for corrosion protection (coating) with “smart” coatings. “Smart” coatings, unlike the classical coatings, which act only as a rigid physical barrier (in some cases with anticorrosion additives, that can move to the coating surface and evolve its beneficial activity), are working as active substrate. The use of capsules (containers, micro or nanocontainers) of various characteristic, filled with different corrosion inhibitors is one of the

most tested methods in the last period for the incorporation of healing agents into anticorrosion coating. Encapsulation of corrosion inhibitor before dispersing them in coatings is essential because the direct application has most contra effects, e.g.: the inhibitor molecules may realize a variety of unwelcome chemical interactions with the components of the coatings, and, as a consequence, the protection properties of the coating might be decreased (Shchukin et al., 2006). For example, triazole and its derivatives are well- known corrosion inhibitors, but in many cases, they cannot be used in epoxy coating because of their high hydrophilic character that can lead to polymer swelling. In order to reduce the solubility of the triazole in water, the triazole can be exposed to plasma-polymerization treatment, when a double-layered structure formed around the inhibitor and this makes it applicable for the epoxy coatings (Yang and Van Ooij, 2004).

There are different ways of inserting corrosion inhibitors in containers. Nanoparticle carriers can fix corrosion inhibitors or they could be encapsulated in nanocontainers; in this case different types of shells around the inhibitors are prepared. There are many ways to use both methods. The inhibitor incorporation into the container depends primarily on the structure of the capsule as well as on the properties of the inhibitor itself. For example, Khramov et al. (2005) incorporated several organic corrosion inhibitors into self-assembled nanophase particle (SNAP). The mercaptobenzimidazole-sulfonate and the thiosalicylic acid, which contain easily ionizable groups are directly inserted in a SNAP, while non-ionizable heterocyclic inhibitors such as mercapto-benzothiazole, mercaptobenzimidazole were incorporated into coatings as inclusion complexes with β-cyclodextrin.

Nowadays, encapsulation of different triazole derivatives (mainly benzotriazole (BTA)), in various types of containers are the focus of many investigations. Layer-by-layer (LbL)-coated silica nanoparticles with polyelectrolyte layer (Shchukin et al., 2006), halloysite nanotubes unmodified or modified by polyelectrolyte bilayers and polyelectrolyte capsules are used as potential nanoreservoirs for BTA (Fix et al., 2009; Jafari et al., 2010; Li et al., 2014; Shchukin and Möhwald, 2007), whereby different encapsulation methods of BTA are possible. Generally, silica nanoparticles are first covered with selected polyelectrolyte layers using LbL methods, then BTA is absorbed as a next layer from acidic media. In order to achieve loading of the BTA molecules into the hybrid nanotubes, the mixture with a saturated solution of BTA is kept under vacuum, and then the tube is covered by polyelectrolyte bilayers (LbL methods).

The thermal-encapsulation methods usually use BTA trapped in polyelectrolyte capsules or the BTA molecules are incorporated into a polyelectrolyte matrix during the polymerization process, which is followed by adsorption of a highly branched polyelectrolyte layer, whose role is the regulation of inhibitor release. In addition to the mentioned nanocontainers, rod-like hematite particles (Kamburova et al., 2014), ZnO modified with polyelectrolyte layers (Sonawane et al., 2012) also serve nanocontainers for BTA.

Besides the BTA, encapsulation of mercapto-benzothiazole (MBT) is one of the most investigated topics, mainly with a goal to improve the protective qualities of epoxy-based coating. This inhibitor can be incorporated in layered double hydroxides (LDHs), anion-exchange polystyrene containers, cerium molybdate nanospheres (CeMo), halloysite nanotubes, silica nanocontainers (SiNC), and silica nanocapsules with mesoporous shells (SiNC) as well as in polyurea microcapsules (Borisova et al., 2012; Kartsonakis et al., 2011; Maia et al., 2016; Maia et al., 2012; Montemora et al., 2012; Shchukin et al., 2008; Tedim et al., 2010). The polystyrene, CeMo and silica containers are usually loaded with MBT using the saturated solution of this inhibitor (in acetone or ethanol), placed into a sealed container under vacuum conditions; while encapsulation of MBT in polyurea microcapsules happens via micro-emulsion oil-in-water in a single step polymerization process. The results show that the polystyrene containers show better effect at earlier immersion stages, while the CeMo container proved to be more useful for longer immersion times.

Cerium molybdate, titanium dioxide, silica armored polystyrene, oligochitosane (eudragit) particles and hydroxyapatite microparticles are applied as nanocontainers for corrosion inhibitor of 8-hydroxyquinoline (8-HQ) (Balaskas et al., 2012; Haase et al., 2012; Kartsonakis and Kordas, 2010; Kartsonakis et al., 2008; Snihirova et al., 2014; Snihirova et al., 2010). During the encapsulation, the saturated solution of 8-HQ in acetone is inserted in the selected nanocontainers and the whole mixture was stirred at room temperature.

Cerium ion is one of the commonly used corrosion inhibitors mainly for protection of aluminum. As a new approach, cerium ions were inserted in zirconium oxide nanoparticles, $CaCO_3$ microbeads or trapped in the form of CeO_2 in linseed oil microcapsules (Selvakumar et al., 2012; Snihirova et al., 2012; Zheludkevich et al., 2005).

In addition to the mentioned corrosion inhibitors, the following compounds in encapsulated form are also can protect metals: polyurethane microcontainers loaded with a mixture of alkoxysilanes synthesized via interfacial polymerization (Latnikova et al., 2011), linseed oil encapsulated into urea–formaldehyde shell (Suryanarayana et al., 2008), ferric nitrate ($Fe(NO_3)_3$) in silica nanocontainers (Ávila-Gonzalez et al., 2011), zinc phosphate nanoparticles, with imidazole core material (Jadhav et al., 2015), dodecylamine inhibitor layers deposited on SiO_2 nanoparticle surfaces (Falcón et al., 2014), etc.

In spite of all favorable features of encapsulated corrosion inhibitors, this mode of metal protection also has some deficiencies. The main disadvantage is the difficulty to encapsulate corrosion inhibitors in appropriate quantity into containers that can ensure the required fully repair of the defect on the coating; other problems are the high price of raw materials and also the multi-step approach in container's preparation.

17.4. Selection of inhibitors: metal dependence *(aluminum, carbon steel and copper)*.

During the last period, different chemicals were investigated as potential corrosion inhibitors for metal, but as it is well known, in most cases the most efficient corrosion inhibitors were organic molecules with hetero atoms in their structure. As has already been mentioned, nowadays the importance of the microcapsules with efficient corrosion inhibiting core materials increases exponentially.

Aluminum alloys are one of the mostly used construction material and opportunity of its "smart" corrosion protection attracts immense attention. The extensively investigated inhibitors for corrosion protection of aluminum alloys in different encapsulated forms are triazole (Yang and Van Ooij, 2004) and thiazole derivatives, mainly benzotriazole (BTA) (Fix et al., 2009; Shchukin et al., 2006) and mercapto-benzothiazole (MBT) (Borisova et al., 2012; Maia et al., 2016; Maia et al., 2012). Other possibility for protection of aluminum alloy is the 8-hydroxyquinoline (Balaskas et al., 2012; Haase et al., 2012; Kartsonakis and Kordas, 2010; Snihirova et al., 2014) and cerium ions (Snihirova et al., 2012; Zheludkevich et al., 2005) encapsulated in different nanocontainers.

Benzotriazole and mercaptobenzothiazole can also effectively protect steel from corrosion (Li et al., 2014; Montemora et al., 2012; Sonawane et al., 2012) like dodecylamine (Falcón et al., 2014), imidazole (Jadhav et al., 2015) and $Fe(NO_3)_3$ (Ávila-Gonzalez et al., 2011) in encapsulated

forms. Benzotriazole, which was a well-known inhibitor against copper corrosion in aqueous environment, lately is also successfully used in encapsulated form as a coating component (Abdullayev and Lvov, 2010; Shchukin et al., 2006).

Many factors determine which inhibitor will be encapsulated and to be built-in a protective coating. Not only the corrosion inhibitive efficacy on the metal which will be coated is important but the compatibility with the shell material, the solubility, the concentration, the toxicity, its price, the rate of release, etc.

17.4.1. Compatibility of inhibitors with shell materials

When we take into account the great diversity in chemical properties of the corrosion inhibitors at one side, and in the characteristics of the known nanocontainers on the other side, it is very important to be familiar with their physicochemical properties in order to make the adequate combination of inhibitor and nanocapsules, respectively, and to achieve the best compatibility between them. Thereby, the following facts must be taken into account: shell materials must protect the incorporated corrosion inhibitors against external influences such as various coating components (additives, fillers, pigments) as well as against environmental impacts, like moisture, oxygen, UV light. However, the shell materials (Scharf et al., 2014) should not block or decrease the protecting properties of the encapsulated corrosion inhibitor in any way. Additionally, vital is, that the shell materials of the selected nanocontainer must be able to prevent premature diffusion of the corrosion inhibitor into the coating; but when damage or any other outer impact influence the coating, the shell material must release the inhibitor into the damaged area.

More recent studies on the evaluation of the best combinations of shell materials and corrosion inhibitors have applied computer-based simulation (Scharf et al., 2014). The advantage of this method lies in the possibility of very fast and cheap testing of the interactions between several types of shell materials and different inhibitors.

17.4.2. Release of inhibitors from the capsules in the self-healing process.

Self-protecting coatings, which contain embedded micro- or nano-containers filled with a corrosion inhibitor, can be used to autonomously defend metals from surface deterioration such as corrosion. The amount of corrosion inhibitor needed to protect the metal surface is related to

the formation of the physically or chemically adsorbed monolayer on the damaged surface thus the size and quantity of containers embedded into the coating can actually be reasonably low. In this condition, there's no need to cover the scratch completely, the inhibitor adsorbed onto the scratch's bare metal surface can safely mitigate the further development of corrosion (Grigoriev et al., 2014).

The rate of release of the active load is dependent on the structure, chemical and acidic /alkaline properties of the passive matrix (Amondola and Meneghetti, 2012).

The discharge mechanism of encapsulated corrosion inhibiting agents differs depending on the structure of the transporter (carrier). Matrix type particles employed in an aqueous environment with specified parameters, such as temperature, pH, and ionic strength, possess certain amount of water depending on their structure which allows continuous leaching of the active agents through diffusion (Telegdi et al., 2014, Mittal, V., 2014).

In the case of core-shell capsules, the release of the inhibitor from the capsule is possible on different ways, e.g. when the coating with capsules is mechanically damaged. The broken capsule releases the entire active inhibiting agent very fast in a non-controllable way. Shell permeability ought to be adjusted by the hydro-phobic/-phylic monomers ratio or capsule shell thickness (Zheludkevich, 2009).

Inhibiting agents discharge rates from microcapsules and solid spheres tend to decrease with time however the amalgamation of encapsulated and free substances in the paint may lead to an equilibrated flux of the active agent (Telegdi et al., 2014).

Nano-container is one of the main approaches for self-healing coatings applied for loading of active inhibiting agents with shell possessing controlled permeability specific to several triggers (Grigoriev et al., 2017). Being homogeneously distributed in the passive matrix, these nano-containers retain the active inhibiting agent in confined state evading undesirable interaction between the active agent element and the matrix as well as spontaneous outburst. When the local parameters suffer changes or the protecting coating is damaged by an external impact, the nano-containers react spontaneously and release the encapsulated active inhibiting agents.

Nano-containers that are pH sensitive are especially suitable for responsive anticorrosion effects, because they provide rapid inhibitor release and protection in response to acidic as well as basic local microenvironment (Yasakau et al., 2014).

Different trigger classifications are shown in the literature, but most of them are very similar. Cole has described triggers to mechanical, thermal, chemical damages, redox activity or electric fields, complex internal or external triggers (Cole, 2014) while Zheludkevich made a slightly different distribution: desorption controlled release, pH-controlled release, ion-exchange control of release, release of inhibitor under mechanical rapture (Zheludkevich et al., 2012).

During the mechanical triggering (rapture), when a crack destroys the coating, microcapsules are ruptured, the healing agents released and in most cases the presence of the catalyst in the coating initializes the polymerization of the healing agent and the crack on the coating closes (White et al., 2001).

Thermal stimulus initiates the release of healing agent from the zeolites and mesoporous nanocontainers (whose shell was made of polymers with mixed glass transition temperatures) (Cole, 2014; Scharf et al., 2014).

Redox reaction or electric fields can mostly be used as a trigger to release the inhibitor from the capsules whose shell materials are electro active (susceptible to oxidation or reduction) under the given condition (Cole, 2014). Fig. 17.2 illustrates microcapsules filled with corrosion inhibitor (a), and microcapsules emptied due to mechanical damage (b).

The presence of water molecules in the coating is a basic triggering for the release of inhibitor, but in many cases it is not specific enough. In most cases, the corrosion processes are accompanied by the change in the local pH values that belongs to one of the most relevant chemical trigger. Based on the results of various studies, in comparison to all of the applied nanocontainers it is evident that the nanocapsules with polyelectrolyte multilayers have the best pH sensitivity for the release of the inhibitor. For example: Möhwald and coworkers have noticed that when the halloysite nanotubes are coated with polyelectrolyte shells, a much better control over the release of the loaded inhibitor was registered (Shchukin et al., 2007). It was also observed that the increase in alkalinity leads to the release of inhibitor. The disadvantage of the polyelectrolyte multilayer is reflected in its complex preparation process.

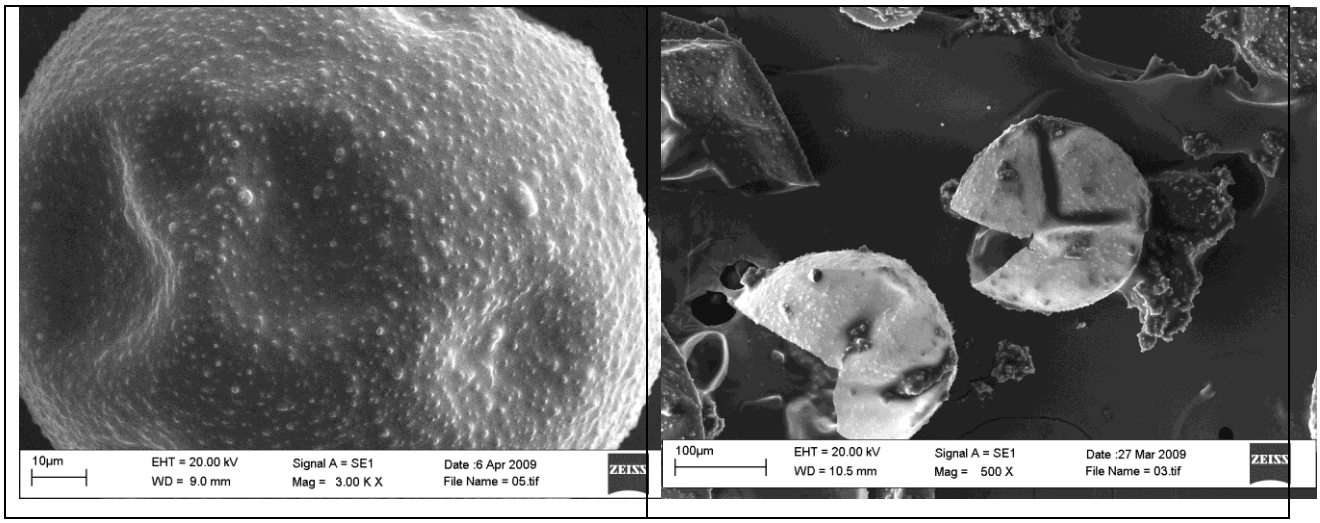

Fig. 17.2 (a,b). Microcapsules filled with corrosion inhibitor (a), and microcapsules emptied due to mechanical damage (b).

Desorption controlled release is the most commonly used as a trigger when, in the nanocapsulation process the inhibitors are absorbed onto the nanoparticles (Zheludkevich et al., 2005). When the coating meets the corrosive environment, water molecules absorb onto the coating and start the degradation of the coating and it also leads to displacement/desorption of the inhibitor molecules from the nanocapsules.

Another efficient method of production of self-healing anticorrosion behavior is the by layer-by-layer assembly (LbL) of polyelectrolyte and corrosion inhibitor either onto or into the different nanoparticles. Depending on the charge on the surface of nanoparticles, a layer of polyelectrolyte can be adsorbed on the surface followed by another layer of oppositely charged polyelectrolyte. It can be followed by adsorption of a layer of corrosion inhibitor. Corrosion activity in the local area leads to the change in pH which causes the opening of the polyelectrolyte layer, allowing the discharge of corrosion inhibitor in the local vicinity. Once the corrosion process is healed, the pH recovers to the original value, leading to the shutting of polyelectrolyte shell and thus stopping the discharge of corrosion inhibitor. Therefore, the inhibitor is released only to heal the corrosion process, thus extending the valuable life of the protective coating (Scharf et al., 2014).

The best nanocapsules are when ion-exchange control initializes the release of inhibitors from nanocontainers of Layered Double Hydroxides (LDHs) structures (Zheludkevich et al., 2012). Corrosion inhibitors in anionic form are located among the positive LDHs layers. During the

contact with aggressive media, the anions present in the corrosive solution displace the inhibitors from the LDHs layers and they replace them. Some inhibitors exist in anionic form only at determined acidity, and, because of that, the changing pH values may also be indirectly considered as triggers.

The future triggers for inhibitor release based on expectations will be various complex systems with internal or external triggers, whose activation will rely on the information provided by the sensors, which are embedded in the coating or applied directly on the protected material.

Several briefly discussed cases will illustrate the mechanisms of self-healing of coating. The application of conductive polymers, like polyaniline (PANI), results in an internal sacrificial electrode formation, which provides protection to the underlying metal substrate. Integration of nanoparticles in the PANI matrix, during formation, can improve the barrier properties of the coatings in addition to the self-healing influence. PANI does not dissolve in common organic solvents, and can therefore be ground to form nanoparticles which can then be incorporated into other polymer matrices (Scharf et al., 2014, Mittal, V., 2014).

Another case is the application of self-healing anti-corrosion coatings that incorporate capsules of catalyst as well as healing agent are uniformly distributed in the organic matrix. The damage to the coating leads to the rupture of these capsules, leading to the mixing of catalyst and healing agent in the damaged region. This results in formation of cross-linked material at the damage site, which results in the healing of the defect.

Biopolymers like chitosan are also known to have self-healing anti-corrosion properties. In this case, if UV light is shone on the polymer chains in the damaged area, they start to form hydrogen bonds with each other and also the substrate, leading to healing of the defect in less than an hour (Scharf et al., 2014, Mittal, V., 2014). The combination of chitosan with nanoparticles can additionally lead to the generation of thermally stable and mechanically firm coatings, which not only demonstrate the self-healing anticorrosion effect, but are also protective towards mechanical and thermal damages.

17.4.3. Compatibility of shell materials with other coating components.

One of the most important features of corrosion inhibitors in capsules are that they could be used as “self-healing” agents in the anticorrosion coating, and they must be compatible with the

coatings. Respectively, the shell materials of the inhibitor containers must not affect (decrease) the important properties of the anticorrosion coatings such as: optimum barrier properties, good adhesion, low moisture permeability, chemical resistance, flexibility, impact resistance, easy application, durability. The inhibitor container (capsule) must not be damaged by the paint components; it must resist solvents, additives, pigments or coating fillers and also must be able to withstand to unexpected effects during normal handling such as storage, coating preparation, weather conditions. However, on the other hand, inhibitor container must register damage emerged on the coating and consequently the capsule shell must break and release the active compound into the damaged area (Scharf et al., 2014). In each individual case, the properties of capsules and the used coating must be harmonized. For example, some polymeric nanocontainers show very good compatibility with the organic epoxy coatings, but in the case of sol–gel inorganic coatings their very poor compatibility was described (Wei et al., 2015). On the other hand, the inorganic clay based nanocapsules (such as layered double hydroxide nanocontainers), significantly improve the corrosion protective properties of the commercial non-inhibited water-based epoxy coating.

17.5. Evaluation of self-healing activity of micro- and nano-capsules filled with inhibitors.

The evaluation of inhibitor-containing microcapsules usually utilizes several techniques in order to quantify the effectiveness of the microcapsules against the corrosion of metals, to study the morphological changes of the surface and the protection mechanism and the healing rate. To achieve those tasks several types of evaluation methods are applied (Binder, 2013).

17.5.1. Non-electrochemical techniques (*visualization techniques*)

17.5.1.1 Optical Microscopy

Optical microscopy, probably the oldest and most versatile scientific technique in material characterization, is an important tool for qualitative evaluation of self-healing materials. The main advantage of conventional optical microscopy is the wide range of magnifications and the relative ease of use, both for *ex situ* and *in situ* monitoring. A relevant limitation of optical microscopy is the resolution determined by the wave length.

Optical microscopy was applied to investigate the self-healing behavior of steel coated with epoxy containing linseed oil encapsulated in phenol-formaldehyde microcapsules (Jadhav et al., 2011). Digital images can provide a quick assessment of the viability of a particular self-healing system, the extent of corrosion can be difficult to quantify, especially if released self-healing chemicals alter the appearance of the coating.

17.5.1.2. Characterization of microcapsules by scanning microscopic techniques.

The microcapsules could be characterized by different techniques. As to the size and its distribution the first one can do is the determination of the average diameter and the size distribution. Different microscopic techniques allow the determination of these parameters like optical, fluorescence, scanning electron-microscope (SEM), transmission electron-microscope, atomic force microscopy (AFM; which could image the shell surface in some nm range), as well as light scattering methods. In most cases the shell wall thickness is also important factor; the SEM or AFM techniques inform us about this parameter. The composition of the shell wall and core material as well as the stability of the capsules could be determined by thermal analysis, and infrared and UV spectroscopy as well as in some cases by NMR analysis. Additional information derives from chromatography and atomic adsorption spectroscopy. Mechanical stability and permeability often characterize the microcapsules (Rosiñski et al., 2002).

Scanning (SEM) and environmental scanning (ESEM) electron microscope /Energy-dispersive x-ray (EDX) analyzer

Both types of the scanning microscopes (ESEM and SEM) are advantageous apparatus for assessing the presence of coating films in the specified location on samples. The SEM techniques can't follow *in situ* the morphological change on the damaged coatings and visualize the healing process. The only we can see is how the surface liked before and after the corrosive attack.

SEM was utilized to evaluate the self-healing of epoxy coatings containing polyurethane (PU) microcapsules of hexamethylene-diisocyanate (HDI) (Huang and Yang, 2011), epoxy resins (Zhao et al., 2011), on steel surface and aluminum alloy specimen with and without TiO_2 coating (Yabuki et al., 2011).

The ESEM differs from the SEM in the measure of the vacuum as it works at less strong vacuum. Under these conditions the surface is not totally dehydrated, shows more precisely the corrosion

damage. Fig. 17.3 demonstrates SEM images of twin microcapsules filled with corrosion inhibitor and lensed oil.

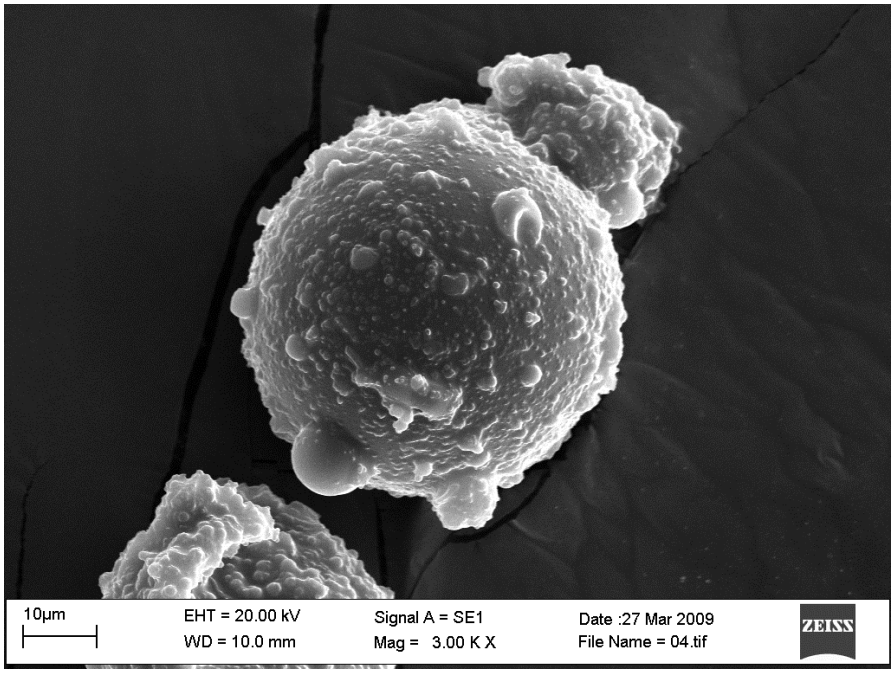

Fig. 17.3. SEM images of twin microcapsules filled with corrosion inhibitor and lensed oil.

17.5.1.3. Confocal laser scanning microscopy (CLSM).

CLSM combines high-resolution optical imaging with depth selectivity, which allows the performance of optical sectioning. CLSM can be used with thick materials and produce images at various penetrations. CLSM can assess the damaged coat sites before and after self-healing. It can produce images of the surface morphology as well as slices of the substrate at different levels. The self-healing character of an intrinsically conducting polymer coating, doped with molybdate ions was analyzed on steel specimen by CLSM technique (Kowalski et al., 2010). The results unequivocally proved the self-healing phenomena.

17.5.1.4. X-ray photoelectron spectroscopy (XPS).

X-ray photoelectron spectroscopy (XPS) is typically performed by exciting the sample surface with mono-energetic Al kα x-rays causing photoelectrons emitted from the sample surface. An electron energy analyzer is used to measure the energy of the emitted photoelectrons. From the binding energy and intensity of a photoelectron peak, the elemental identity, chemical state, and quantity of a detected element can be determined.

The key feature of the XPS technique is that it can detect the chemical species formed before and after the self-healing process which offers valuable data related to reactions and mechanisms of self-healing process.

The self-healing mechanism on a scratched coating of 1,2-bis(triethoxysilyl)ethane containing sodium silicate and cerium nitrate formed on zinc electrode was examined and demonstrated by XPS technique (Aramaki, 2003).

17.5.1.5. Salt spray test (Fog test).

Salt spray testing is an accelerated corrosion method that is widely used for evaluation of coatings before and after treatment with deteriorating environment (ASTM G85-11, 2011). The appearance of corrosion products, coating damages, and the healing of purposely damaged surfaces is assessed after a pre-arranged time period. In the salt spray test sodium chloride solution is pumped into a nozzle where it meets a jet of humidified compressed air, forming a droplet spray. This est is common due to its relative low cost. Its drawback is the weak correlation between the time spent in salt spray test and the expected life of coatings. It means that some coating formulations that gave good result in salt spray test, show worse throughput in the field, and vice versa.

Polymer based nanocapsule developed from methyl diphenyl diisocyanate as core material and urea-formaldehyde as shell material was incorporated into sol-gel matrix for steel coating and the protection at the damage or crack locations was evaluated in 3.5% NaCl solution (Guin et al., 2014). The salt spray blow is often changed by pure water spray and the time span of these handling is predefined. Additionally, between the different influences the coated metal surfaces are allowed to dry.

17.5.2. Electrochemical techniques.

Since metal corrosion is an electrochemical process, electrochemical methods provide powerful tools to evaluate the protection efficiency of the different types of coatings - inclusive of self-healing ones - against corrosive deterioration. There are many common electrochemical techniques that can evaluate inhibition performance of microcapsules. Some will be displayed in more details than others depending on their frequent applications (Fayyad et al., 2014).

17.5.2.1. Open circuit potential (OCP).

The open circuit potential also known as electrochemical corrosion potential (ECP), shows the voltage difference between a metal immersed in a given environment and an appropriate standard reference electrode (SRE). OCP values can provide useful data about the time needed for the system to reach a steady state and the transitions between passive and active states. An example for the use of OCP technique for evaluation of the effectiveness of polypyrrole coating doped with molybdate, used on a carbon steel electrode is when the restoration of the passive state of the steel in NaCl solution was demonstrated (Kowalski et al., 2010; Lehr and Saidman, 2014).

17.5.2.2. Potentiodynamic polarization (PDP).

Potentiodynamic polarization is a technique when the potential of the electrode is varied over a relatively large potential domain at a selected rate by measuring the current flowing through the electrolyte. It provides important information on the corrosion rate, on mechanisms, and on the susceptibility of protecting materials, e.g. coatings, under certain conditions. A PDP variant is cyclic voltammetry, which involves sweeping the potential between two set values, first in a positive then in a negative direction relative to the starting (OCP) potential.

Another type of potentiodynamic polarization is the potentiostatic polarization method, which is a technique for polarizing an electrode in a series of potential steps (ΔE) where the time spent at each potential is constant (Δt), while the current is often allowed to stabilize prior to changing the potential to the next step. The step increase (scan rate) may be small, then the technique resembles to a potentiodynamic scanning curve.

The PDP technique was applied in several studies to evaluate the inhibition efficiency of different polymers coatings on iron electrodes in NaCl solutions (Aramaki, 2002; Yabuki and Okumura, 2012).

The disadvantage of this technique is the voltage drop due to current flow in an electrolyte (concentration polarization and IR drops). These restrictions decrease the usefulness of polarization techniques to evaluate self-healing corrosion performance.

17.5.2.3. Electrochemical impedance spectroscopy (EIS).

Electrochemical impedance spectroscopy (EIS) is a non-destructive technique that determines the dielectric properties of coatings on metals. The principle of this technique is to apply an *AC*

signal of small amplitude to an electrode immersed into an electrolyte. The initial disturbance (applied) and the response of the electrode is compared by measuring the phase shift of the current and voltage components and by the measurements of their amplitudes.

The EIS technique works in the frequency domain and is based on the concept that an interface can be assumed as a combination of passive electrical circuit elements, i.e., resistance, capacitance and inductance. When an alternating current is applied to these elements, the resulting current is obtained using Ohm's law (Binder, 2013). In most cases, data collected by EIS measurement is depicted in Nyquist and Bode plots, for easier interpretation of the results.

One of the most effective applications of EIS has been in the evaluation of the protective properties of polymer coatings and their degradation as a function of exposure time (Mansfeld, 1995).

The self-healing efficiency of microcapsules containing epoxy resin embedded in silicon polymer, acrylic monomers and additives was investigated by EIS (Neema et al., 2013).

Determining the appropriate form of the equivalent circuit, used in modeling the EIS data, is the most challenging task of accomplishing reliable results. This technique allows characterizing numerically the charge transfer resistance (R_{ct}) of the coating which shows the permeability of the film formed at the metal surface. Higher R_{ct} proves the more tightness of the coating that could be the result of the effective function of self-healing nano/microcapsules in the surface film.

The disadvantage of EIS is that it is time consuming, depending on the chosen lower frequency limit. With this method, the system under measurement should be at a constant state throughout the required time to gauge the EIS spectrum. System drift is another disadvantage of EIS measurement and analysis. Modern EIS commercial systems overcame these limitations and tremendously developed over the years (Binder, 2013; Mansfeld, 1995).

17.5.2.4. Scanning vibrating electrode technique (SVET).

The scanning vibrating electrode technique uses a single wire placed near to the surface of coated metal to measures voltage drop in solution. This voltage drop is a result of local current at the surface of a sample. Measuring this voltage in solution images the current at the sample surface. Current can originate from a corrosion process, or the current can be externally controlled using a galvanostat. A solitary electrode is vibrated perpendicular to the surface being studied using a

piezoelectric vibrator. The potential is recorded at the highest and lowest probe positions, resulting in a sinusoidal AC signal. SVET was effectively applied to study the corrosion protection and the self-healing properties of coatings (Bastos et al., 2010; Ogle et al., 2000).

17.5.2.5. Scanning electrochemical microscope (SECM).

A scanning electrochemical microscope (SECM) is a scanning probe technique in which an ultrathin microelectrode tip (UME) is posed in close proximity to another electrode's surface to obtain information about its reactivity: such as through feedback of a redox mediator in solution between the UME and surface or to modify the surface. The UME is attached to highly sensitive motors that can regulate the distance of the UME from the surface or move it laterally to obtain an image of the topography and/or charge transfer near a metal surface (Santana et al., 2010; Souto et al., 2009; Souto et al., 2008).

SECM is an important method for assessing self-healing performance. It is highly specific and can measure smaller and faster phenomena due to its very small probe tip. Furthermore, the surface topography can be recorded by the position of the probe tip (Sun et al., 2007).

The study of self-healing of steel corrosion under scratched epoxy resin with microencapsulated, linseed oil was followed by ECSEM and the corrosion inhibiting activity of coating filled with inhibitor-loaded microcapsules was successfully demonstrated (Pilbath et al., 2012).

17.6. Motivating prospects for the future, multi-level complexity of self-healing.

The materials durability is probably one of the main challenges encountered today for structural as well as coating applications. As the materials failure normally starts at the nanoscale level and is then amplified to the micro- up to the macro-scale level until disastrous failure happens, the ultimate solution would be to prevent and/or abolish damage as it ensues at the nano/microscale and reestablish the original material properties.

Innovative microcapsules of various types from sustainable materials gain more and more attention for application in various smart systems from drug delivery through bioactive surfaces to corrosion protection and further. Incorporation of different functionalities into nano-container shell wall, and into the core will increase the potential of nano-containers for multifunctional materials.

17.7. Summary

T this chapter expands the understanding of different processes and difficulties associated with the applications of micro-/nanocapsules in the inhibition protection of metals through the development of smart self-healing coating systems.

Nowadays, there is a noticeable tendency to use "*smart*" corrosion protection of different materials (metals). The advantage of this lies in the fact that "*self-healing*" coatings can register the emerged crack on the material that leads to activation of encapsulated anticorrosion inhibitor, which can heal the damage.

Though there is a great diversity in chemical properties of the corrosion inhibitors (depending on the metal and the environment) and in the characteristics of the nanocontainers and coatings, it is significant to combine them, with the goal to achieve the best possible protection by anticorrosive coatings under given conditions.

This chapter has summarized the possibilities, which lead to preparation of microcapsules filled with inhibitor(s) together or without a liquid which helps to insulate the metal surface from the outer aggressive environment. As long as this oily core material solidifies, the inhibitor saves the metal surface in intact form from corrosive deterioration. In most cases, the core material with oily liquid and inhibitor fulfill both requirements: they diffuse along the damaged gap, start to solidify via polymerization and, at the same time, confine the undesired corrosion reactions.

The most important shell and core materials were summarized and the importance of the material compatibility between the shell and the core as well as the shell and the other components of the paint were demonstrated. Comprehensive review has discussed the techniques that allow the synthesis of microcapsules with different shell and core materials and give account about the importance of the reaction conditions (temperature, pH, concentration, stirring speed etc.) that allow the preparation of capsules with predefined characters (size, size distribution, ion strength, covering layer etc.). The combination of all these factors realizes in elaboration of proper nano- and microcapsules for multifunctional protective coatings.

Summarizing the possible self-healing activities, the classification of different trigger mechanisms are the follows:

- mechanical triggering (rapture),
- thermal stimulus,

- chemical damage,
- redox reaction or electric fields,
- complex internal or external trigger,
- water,
- pH sensitivity,
- pH-controlled release,
- desorption controlled release,
- Ion-exchange controlled release.

All these possible mechanisms are discussed in details above. The most important is to be sure that the healing material will be released on demand, i.e. when the environment changes, the chemicals that help in curing the injured coatings will be released and they will fulfill their function.

Self-healing coatings are a robust method of corrosion protection that can autonomically restore damage and extend the life expectancy of the coating. Evaluation of the performance of self-healing coatings can be performed either globally or locally by several methods that range from visualization to electrochemical information. The focal drawbacks of the techniques applied in evaluation of self-healing inhibiting performance are mainly the follows: unease in obtaining a stable potential, as in case of OCP; restrictions arising from the concentration polarization and IR drops, as in PDP; and difficulty in the proper buildup of the equivalent circuits, as in the EIS. The electrochemical techniques PDP and EIS provide quantitative outcomes about the self-healing development, where corrosion rates and inhibition efficiency provided by self-healing capsules embedded into coatings can be determined by them. These methods provide general data about the self-healing process and do not provide details of the reactions taking place locally at the crack site. Other methods that can follow the processes occurring locally at the solid-liquid interfaces (as in the case of SVET) may provide hints in studying the mechanisms of the related EC reactions and the involved active species.

Different scanning microscope methods, such as AFM, SEM, supply information on capsule's size and its distribution as well as on mechanistic details about the self-healing process. In addition, XPS and EDX can chemically analyze the different materials formed upon self-healing process.

It is recommended to combine local and global electrochemical techniques with the non-electrochemical devices to get a more complete depiction of the self-healing performance including the mechanisms involved in the complex processes of the self-healing.

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